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Description

This invention relates to liquid detergent compositions and especially to so-called light duty liquids intended primarily for dishwashing. More particularly the invention concerns dishwashing liquid detergent compositions that have been formulated to secure improved particulate soil removal ability without any loss in other performance areas such as grease and oily soil removal and sudsing capability.

The greasy and/or oily nature of the majority of food residues has resulted in grease and oily soil removal being the prime focus of dishwashing detergent performance, together with the need to provide a satisfactory volume of suds over the duration of the dishwashing task. This has been reflected in the composition of liquid detergent products formulated primarily or exclusively for dishwashing, such products conventionally comprising a combination of one or more surfactants and suds builders dissolved or dispersed in a hydrotrope-water system.

Dishwasing liquid detergent formulations of this type include magnesium salts and magnesium surfactants such as alkyl sulphates, alkyl ether sulphates and alkyl benzene sulphonates and GB—A—1,524,441, 1,551,074, 2,010,893A and EP—A—0039110 are representative disclosures of the state of the art. The art teaches that these formulations have enhanced performance, particularly when used in water of low mineral hardness. Dishwashing liquid detergent compositions containing alkane and alkene sulphonates are also known, examples of such disclosures including those in GB—A—1,050,848, 1,339,069, 1,382,295, 1,451,228, 1,551,074 and 1,567,421.

Formulations of this type employing total surfactant levels in excess of 25% by weight cannot tolerate significant levels of inorganic detergent builder salts whilst retaining a clear single phase solution form and additionally, the presence of inorganic salts gives rise to aesthetically undesirable residues on the washed crockery or cutlery. Consequently, these formulations are normally substantially completely free of detergent builder salts, while metal chelating agents, if incorporated, are only employed in trace amounts.

Nevertheless, particulate materials are also a significant component of food residues and the low levels, or total absence, of detergent builder materials in conventional dishwashing liquid detergents make these formulations less than optimum in terms both of suds stability in the presence of particulate soil and of particulate soil suspension during the washing process. It has now been found that, certain combinations of ingredients, more particularly an alkali earth metal alkyl sulphate and an ethoxylated alcohol, can provide an unexpected improvement in particulate soil handling capability without any sacrifice of the grease and oily soil removal performance of a dishwashing liquid formulation.

The employment of ethoxylated alcohols as components of dishwashing liquids is known in the art, exemplified by GB—A—1,567,421 and GB—A—1,551,074. However, the benefit asserted for their inclusion is principally in the area of suds boosting and, to a lesser extent, greasy soil removal. Moreover the utilisation of ethoxylated alcohols in dishwashing liquids is limited by the increase in chill point temperature which they cause. For example, their incorporation into formulations such as are disclosed in EP—A—0039110 results in products that show an insignificant performance benefit together with totally unacceptable stability characteristics. Thus the finding that the compositions of the invention have particulate soil removal efficacy together with acceptable physical characteristics is the more unexpected.

According to the present invention therefore there is provided a clear homogeneous magnesium containing liquid detergent composition having a chill point of not more than 5°C comprising a surfactant mixture in a hydrotrope-water system, characterised in that the surfactant mixture is formed by the combination of

a) a water soluble C_{13}—C_{18} alkane or C_{12}—C_{16} alkene sulphonate,

b) a water soluble alkyl polyethoxy sulphate wherein the alkyl group contains from 10 to 16 carbon atoms and the polyethoxy group contains an average of from 0.5—6 ethoxy groups,

c) 2.0—5.0% by weight of the composition of an ethoxylated primary C_8—C_{12} alcohol having an HLB in the range 7.5—12.0,

d) 6—18% by weight of the composition of a primary C_{10}—C_{16} alkyl sulphate,

the composition comprising the magnesium ion in an amount corresponding to 0.40X—0.60X, where X is the molar amount of said primary C_{10}—C_{16} alkyl sulphate.

The present invention comprises a surfactant system containing paraffin or olefine sulphonate, alkyl ether sulphate, alkyl sulphate and ethoxylated nonionic surfactant components in a liquid vehicle composed of hydrotrope and water.

The alkyl sulphate surfactant component is a primary alkyl sulphate in which the alkyl group contains 10—16 carbon atoms, more preferably an average of 12—15 carbon atoms preferably in a linear chain. C_{10}—C_{16} alcohols, derived from natural fats or Ziegler olefin build-up or oxo synthesis, form suitable sources for the alkyl group. Examples of synthetically derived materials include Dobanol 23 (RTM) sold by Shell Chemicals (UK) Ltd, Ethyl 24 sold by the Ethyl Corporation, a blend of C_{13}—C_{15} alcohols in the ratio 67% C_{13}, 33% C_{15} sold under the trade name Lutensol by BASF GmbH and Synperonic (RTM) by ICI Ltd, and Lial 125 (a highly branched C_{12}—C_{15} primary alcohol) sold by Liquichimica Italiana. Examples of naturally occurring materials from which the alcohols can be derived are coconut oil and palm kernel oil and the corresponding fatty acids.

The alkyl sulphate component is present at a level of from 6% to 18% by weight of the composition, more generally from 8% to 16% by weight.

For the purposes of the present invention the alkyl sulphate is associated with a source of magnesium ions which, as will be described hereinafter, can either be introduced as the oxide or hydroxide to neutralise the acid or can be added to the composition as a water soluble salt. However, the addition of appreciable levels of magnesium salts to the dishwashing compositions of the invention raises the temperature at which inorganic salt crystals form in the compositions on cooling and is therefore less preferable. The molar amount of magnesium ion in the compositions is controlled to correspond to 0.40—0.60X preferably 0.45—0.55X where X is the number of moles of C_{10}—C_{16} alkyl sulphate present. Most preferably the magnesium ion content is adjusted to provide the stoichiometric equivalent of the alkyl sulphate present. In practice the magnesium ion will be present at a level of from 0.15% to 0.70% by weight, preferably from 0.35% to 0.60% by weight of the composition.

The paraffin sulphonate (s-alkane sulphonate), or α-olefine sulphonate (alkene sulphonate) component comprises from 3% to 15%, more preferably from 4% to 12% by weight of the formulation.

Secondary alkane sulphonates useful in the present invention preferably have from 13 to 18 carbon atoms per molecule, and most desirably from 14 to 17, and are characterised by a high solubility in water compared to alkyl aryl sulphonates and other sulphuric acid reaction products used for dishwashing detergent compositions. These sulphonates are preferably prepared by subjecting a cut of paraffin, corresponding to the chain lengths specified above, to the action of sulphur dioxide and oxygen in accordance with the well-known sulphoxidation process. The product of this reaction is a secondary sulphonic acid which is neutralized with a suitable base to provide a water-soluble secondary alkyl sulphonate. Similar secondary alkyl sulphonates may be obtained by other methods, e.g. by the sulphochlorination method in which chlorine and sulphur dioxide are reacted with paraffins in the presence of actinic light, the resulting sulphonyl chlorides being hydrolyzed and neutralized to form the secondary alkyl sulphonates. Whatever technique is employed, it is normally desirable to produce the sulphonate as the monosulphonate, having no unreacted starting hydrocarbon or having only a limited proportion thereof present and with little or no inorganic salt by-product. Similarly, the proportions of disulphonate or higher sulphonated material will be minimized but some may be present. The monosulphonate may be terminally sulphonated or the sulphonate group may be joined on the 2-carbon or other carbon of the linear chain. Similarly, any accompanying disulphonate, usually produced when an excess of sulphonating agent is present, may have the sulphonate groups distributed over different carbon atoms of the paraffin base, and mixtures of the monosulphonates and disulphonates may be present.

Mixtures of monoalkane sulphonates wherein the alkanes are of 14 and 15 carbon atoms are particularly preferred wherein the sulphonates are present in the weight ratio of C_{14} to C_{15} paraffins in the range from 1:3 to 3:1, preferably 1:2 to 2:1. Surprisingly, this particular mixture produces detergents which clean dishes better and which suds longer, especially in hard water, than other mixtures of paraffin sulphonates, e.g. those of 13 to 17 carbon atoms. This is also true, to a lesser extent, of the individual components of the C_{14} and C_{15} mixture.

The term 'α-olefine sulphonates' or 'alkene sulphonates' is used herein to mean compounds which can be produced by the sulphonation of alpha-olefines by means of uncomplexed sulphur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolysed to give the corresponding hydroxy-alkane sulphonates. The sulphur trioxide may be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2, etc., when used in the gaseous form.

The alpha-olefines from which the olefine sulphonates are derived are mono-olefines having 12 to 16 carbon atoms, preferably 12 to 14 carbon atoms. Preferably, they are straight chain olefines. Olefine sulphonates having more than 16 carbon atoms do not give the desired high lathering performance in the mixtures according to the invention; those with fewer than 12 carbon atoms have reduced detergent properties. In addition to the true alkene sulphonates and a proportion of hydroxy-alkane sulphonates, the olefine sulphonates may contain minor amounts of other materials, arising from impurities in the original olefine stock and from side reactions during the sulphonation and neutralisation processes.

The alkyl ether sulphate component comprises a primary alkyl ethoxy sulphate derived from the condensation product of a C_{10}—C_{16} alcohol with an average of from 0.5 to 6 ethylene oxide groups. The C_{10}—C_{16} alcohol itself can be obtained from any of the sources previously described for the alkyl sulphate component. It has, however, been found preferable to use alkyl sulphate and alkyl ether sulphate in which the carbon chain length distributions are the same. C_{12}—C_{15} alkyl ether sulphates are preferred and the level of alkyl ethoxy sulphate in the compositions lies between 0.5% and 20% by weight of the compositions, generally in the range from 4% to 14% by weight.

The conventional average degree of ethoxylation is from 0.5 to 3 groups per mole of alcohol, but as conventional ethoxylation processes result in a distribution of individual ethoxylates ranging from 1 to 10 ethoxy groups per mole of alcohol, the average can be obtained in a variety of ways. Blends can be made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation. In fact, it has been found that equivalent sudsing and grease removal performance to that given by a blend of alkyl sulphate and alkyl ethoxy ether sulphate can be obtained by reducing the overall level of ethoxylation and

using an alkyl ether sulphate in which the ratio of ethoxylated to unethoxylated alkyl sulphate is the same as would be obtained by mixing the separately prepared surfactants.

The cations, other than magnesium, that may be used in the neutralisation of the anionic surfactants may be sodium, potassium, ammonium or alkanolammonium, but ammonium is a preferred cation because of its depressive effect on the chill point temperature of the compositions. Preferred compositions have chill points of less than 0°C.

The surfactant system also comprises an ethoxylated C_8—C_{12} primary alcohol having an HLB (hydrophilic-lipophilic balance) in the range from 7.5 to 12.0, preferably from 8.0 to 9.5. The primary alcohol may be linear or branched in structure and can be derived from sources such as those described in connection with the alkyl sulphate component. Preferred materials are those in which the alcohol is derived from a C_9—C_{11} hydrocarbon fraction in which the hydrocarbon material contains up to 25% methyl branching, and the level of ethoxylation provides an average of 2—3, more preferably 2.5 ethoxy groups per mole of alcohol.

Typical composition ranges for the surfactant combinations described above are

6—10%	C_{12}—C_{13} alkyl sulphate
8—12%	C_{12}—C_{13} alkyl $(EO)_2$ sulphate
8—12%	C_{14}—C_{17} paraffin sulphonate
2.0—3.0%	C_9—C_{11} $(EO)_{2.5}$
12—16%	C_{13}—C_{15} alkyl sulphate
4—8%	C_{13}—C_{15} alkyl $(EO)_2$ sulphate
4—8%	C_{14}—C_{17} paraffin sulphonate
2—4%	C_9—C_{11} $(EO)_{2.5}$
16—22%	C_{13}—C_{15} alkyl $(EO)_{0.5-1.0}$ sulphate*
4—8%	C_{14}—C_{17} paraffin sulphonate
2—4%	C_9—C_{11} $(EO)_{2.5}$

A desirable optional component of the invention is a suds boosting agent at a level of up to 5%, preferably from 3% to 4% by weight.

The suds-promoting agent may be selected from C_{12}—C_{14} mono- and di-C_2—C_3 alkanolamide, C_{12}—C_{14} alkyl amides condensed with up to 15 moles of ethylene oxide per mole of amide and tertiary amine oxides containing a C_8—C_{18} alkyl group.

Examples of the alkanolamides are coconut alkyl monoethanolamide, coconut alkyl diethanolamide and coconut alkyl mono and di isopropanolamides.

Examples of the ethoxylated amides include coconut alkyl amide condensed with an average of six moles of ethylene oxide, lauryl amide condensed with an average of eight moles of ethylene oxide, myristyl amide condensed with an average of ten moles of ethylene oxide and coconut amide condensed with an average of eight moles of ethylene oxide. Amine oxides useful in the present invention have one alkyl or hydroxyalkyl moiety of from 8 to 18 carbon atoms, preferably from 8 to 16 carbon atoms and two moieties selected from alkyl groups and hydroxyalkyl groups containing 1 to 3 carbon atoms. Examples of such amine oxides include dimethyl octylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, methylethyl hexadecylamine oxide, and dimethyl-2-hydroxyoctadecylamine oxide.

A highly preferred example of the tertiary amine oxide is a C_{12}—C_{14} alkyl dimethyl amine oxide in which the C_{12}—C_{14} alkyl group is derived from coconut oil.

The balance of the formula comprises a hydrotrope-water system in which the hydrotrope may be urea, a C_1—C_3 alkanol, or a lower alkyl benzene sulphonate salt such as toluene, cumene or xylene sulphonate. The preferred hydrotrope is ethanol which is employed at from 3% to 10% by weight of the composition, preferably at from 4% to 8%.

Optional ingredients of the liquid detergent compositions of the invention include thickeners such as guar gum, antibacterial agents such as glutaraldehyde and Bronopol (RTM), antitarnish agents such as

* This corresponds to 12—16% alkyl sulphate and 4—6% of an ethoxylated C_{13}—C_{15} alkyl sulphate having an average degree of ethoxylation of approximately 2.

benzoxytriazole, heavy metal chelating agents such as EDTA or EDTMP, perfumes and dyes. The pH of the compositions may be anywhere within the range from 6 to 7.5 but as manufactured the compositions normally have a pH in the range from 6.6 to 7.3, preferably from 6.6 to 6.9 in order to maintain colour stability.

The technique of incorporation of the magnesium ions is not thought to be critical and the compositions can be made in a number of ways.

The individual anionic surfactants can be made as aqueous solutions of alkali metal or ammonium salts which are then mixed together with the hydrotrope, and the suds booster, if this is included, following which the magnesium ion can be introduced as a water soluble salt such as the chloride or acetate. Optional minor ingredients are then added after which the pH and viscosity is adjusted. This method has the advantage of utilising conventional techniques and equipment but results in the introduction of additional chloride or acetate ions which can increase the chill point temperature (the temperature at which inorganic salts precipitate as crystals in the liquid).

An alternative method of carrying out the invention is to mix the alcohol and alcohol ethoxylate together and carry out a single sulphation and neutralisation. For this, the alcohol and alcohol ethoxylate should be mixed in a weight ratio lying in the range 45:1 to 1:5.5. Sulphation can take place by means of any of the conventional sulphating agents such as e.g., sulphur trioxide or chlorosulphonic acid. Neutralisation of the alkyl ether sulphuric acid and the alkyl sulphuric acid is carried out with a magnesium oxide or hydroxide slurry which avoids the addition of chloride or sulphate ions. Although not essential, it is convenient to use a mixture of these acids as the magnesium salt of the alkyl ether sulphuric acid has relatively greater aqueous solubility than the alkyl sulphuric acid component. The separately neutralised paraffin sulphonate salt, and the neutralised alkyl and alkyl ether sulphate salts and the hydrotrope are then added to the final mixing tank and the C_8—C_{12} alcohol ethoxylate and any optional ingredients added before the pH is adjusted as above.

A further and preferred modification of the above technique involves the preparation of a single alcohol ethoxylate feedstock whose composition is the same as, or closely approximates that of, the alcohol and alcohol ethoxylate blend. For the purposes of the present invention alcohol ethoxylates having an average degree of ethoxylation in the range 0.5 to 1.0, more usually 0.75 to 0.95 are preferred.

Modifications of this latter technique can also be employed in which either the neutralised paraffin sulphonate salt or the neutralised alkyl sulphate-alkyl ether sulphate mixture are used as a 'heel' for the neutralisation of the acid form of the other, thereby avoiding local overheating, formation of viscous phases etc.

The invention is illustrated in the following examples in which the percentage of the components are by weight based on the finished composition.

Example I

The following composition was made up.

C_{13-15} alkyl sulphate[1]	8.6	incorporating 0.47 parts NH_4^+ ion, 0.78 parts Na^+ ion and 0.34 parts Mg^{++} ion, the level of Mg^{++} corresponding to 0.5X where X is the number of moles of alkyl sulphate
C_{13-15} alkyl $(EO)_2$ sulphate[2]	10.4	
C_{14-17} paraffin sulphonate	10.7	
Dobanol 91$\bar{E}_{2.5}$[3]	2.7	
Narrow cut coconut monoethanolamide	4.0	
Ethanol	5.0	
Perfume, Colour & Misc.	1.0	
Water	to 100	

[1] Derived from Synperol 35 (RTM) a C_{13}—C_{15} primary alcohol sold by ICI Ltd.
[2] Derived from Synperol 35 (RTM) primary alcohol condensed with an average of two ethylene oxide groups per mole of alcohol.
[3] A C_9—C_{11} primary alcohol condensed with an average of 2.5 ethylene oxide groups per mole of alcohol. Sold by Shell International Chemicals Ltd.

The paraffin sulphonate was performed by SO_2 sulphonation of C_{14}—C_{17} n-alkanes and caustic soda neutralisation of the resultant sulphonic acid to give an approximately 60% active paste starting material. This was diluted with water and a little ethanol to form a 30% active solution in which the monoethanolamide was dispersed with agitation to assist its solution. A blend of the alcohol and alcohol ether

condensate was sulphated using chlorosulphonic acid as the sulphating agent and the mixed sulphuric acids were then neutralised with magnesium hydroxide and ammonia respectively. The actual neutralisation (to pH 3.0) was carried out using a 'heel' formed by the diluted paraffin sulphonate paste, in which the ammonia and magnesium hydroxide were dispersed before addition of the mixed sulphuric acids. The pH was then trimmed to pH 6.6 with ammonia before the ethoxylated nonionic and other minor ingredients (dye, perfume) were added to form the final composition. The finished product had a viscosity of 0.23 Pa·s at 20°C and a chill point of −3°C.

Example II

The following composition is prepared using the same materials as in Example I.

C_{13-15} alkyl sulphate	14.0	incorporating 0.28 parts NH^{+}_{4} ion, 0.41 parts Na^{+} ion and 0.57 parts Mg^{++} ion, the level of Mg^{++} corresponding to 0.5X where X is the number of moles of alkyl sulphate
C_{13-15} alkyl $(EO)_2$ sulphate	6.0	
C_{14-17} paraffin sulphonate	6.0	
Dobanol $91E_{2.5}$	3.5	
Narrow cut coconut monoethanolamide	4.0	
Ethanol	6.0	
Minors	1.3	
Water	61.2	

The n-paraffin is sulphonated and neutralised to produce the sodium paraffin sulphonate as in Example I. The blend of C_{12}—C_{13} alcohol and C_{12}—C_{13} alcohol ethoxylate are sulphonated using gaseous SO_3 and are then neutralised by addition to an ethanol water mixture in which the ammonia and magnesium hydroxide have been dispersed. Further ethanol, the amide and C_9—C_{11} alcohol ethoxylate are added to this mixture together with paraffin sulphonate salt. Perfume, colour and pH trimming acid forming the minor components are then added to complete formation of the product which has a chill point of −3°C.

Example III

Four liquid detergent formulations were prepared having the following compositions. Formulations A, B and C are commercially available liquid detergent products while formulation D is in accordance with the invention.

	A	B	C	D
Mg C_{12}—C_{15} alkyl sulphate	9.6	8.6		8.6
NH_4C_{12}—C_{15} alkyl $(EO)_3$ sulphate	11.4			
NH_4C_{12}—C_{15} $(EO)_2$ sulphate		10.4		10.4
NH_4C_{12}—C_{15} $(EO)_{1.5}$ sulphate			5.5	
Na C_{14}—C_{17} paraffin sulphonate			35.3	10.7
$NH_4C_{11.8}$ alkyl benzene sulphonate	14.2	14.2		
Coconut Monoethanolamide	4.0	4.0		4.0
C_9—C_{11} primary alcohol $(EO)_{2.5}$				2.7
C_9—C_{11} primary alcohol $(EO)_{4.0}$			2.7	
Ethanol	8.0	8.3	3.0	5.0
Urea			1.2	
Perfume & Miscellaneous	1.0	1.0	2.6	1.3
Water		to 100		

A series of comparative evaluations of the above formulations were run using the mechanical sudsing test method described below.

This method uses 4 cylinders of length 30 cm and diameter 10 cm fixed side by side, and rotatable at a speed of 24 rpm about a central axis. Each cylinder is charged with 500 ml of product solution at a concentration of 0.12% and a temperature of 45°C. The outer two cylinders are used for one of the products being compared and the inner two for the other product.

The cylinders are rotated for 2 minutes, stopped, the initial suds are measured and a soil load is then added. The grease soil comprises a mixture* of fatty acids in a cooking oil base and 1 ml of this mixture (MFFA) is added to each cylinder. Where particulate soil is included it is all added at this stage. After 1 minute the cylinders are restarted and allowed to rotate for 1 minute. The suds height is noted and 1 ml of the 2% MFFA is added to each cylinder. After 1 minute the cylinders are restarted. This process continues until the suds height in the cylinder is lower than 0.5 cms.

* The grease soil comprised:

2 parts oleic acid
2 parts linoleic acid
1 part stearic acid
2.5 parts palmitic acid
367 parts pure corn oil to give a 2% Mixed Free Fatty Acid (MFFA) mixture

One product is designated as the control and suds and mileage figures are calculated for the other product versus the 'control' product on the following basis.

$$\text{Suds of test product} = \frac{\text{Total amount of suds produced by test product up to and including when suds reduced to 0.5 cm}}{\text{Total amount of suds produced by control product up to and including when suds reach 0.5 cm}} \times 100$$

$$\text{Mileage of test product} = \frac{\text{number of soil additions to test product solution to reduce suds height to 0.5 cm}}{\text{number of soil additions to control product to reduce suds height to 0.5 cm}} \times 100$$

Mileage figures of comparisons made using this test were as follows, the second-identified product in each instance constituting the 'control'.

	2°H	18°H
B vs A[1]	106	101
C vs A[2]	39	57
C vs B[2]	59	47
D vs B[2]	125	110

Suds figures of a comparison made between products D and B were as follows:

D vs B[2]	119	109

[1] The figures quoted are an average over a range of particulate — grease soil mixtures including (i) 5 g cake mix (McDougalls Sponge Mix), 2% MFFA, (ii) 5 g gravy/flour, 2% MFFA, (iii) 5 g potato powder, 2% MFFA.
[2] The figures quoted are for a 5 g cake mix, 2% MFFA soil mixture.

On the basis of the above tests it can be seen that the ranking of the formulations, in terms of their mileage performance is

$$D > B \geqslant A \gg C$$

where D is a formulation in accordance with the invention. Moreover the above data also shows that the sudsing performance of formulation D in the presence of particulate soil is significantly better than that of formulation B.

In a further mileage evaluation, using soil (2) above, formulation B was compared to formulation D and also to a formulation D' from which the ethoxylated primary alcohol component was omitted.

The results are shown below, with formulation B serving as the 'control' and being expressed as 100.

	2°H	18°H
D vs B	125	110
D' vs B	100	105

The benefit conferred by the incorporation of the nonionic component can be clearly seen.

Example IV

Comparisons were made of the soil suspension performance of the formulations D & B of Example III using the following test method.

Two 2 litre beakers were each charged with 1500 ml of soft water (2°H) at a temperature of 40°C. A magnetic stirrer was placed in each beaker and activated, the stirring mechanisms being adjusted so that both beakers were being stirred at the same rate. 20 g of cake mix, 15 ml of 2% MFFA and the desired weight of the detergent product were weighed into each beaker, one product being the 'test' product and the other forming the 'standard'. The solutions were then stirred for approximately 15 minutes (to allow a homogeneous solution to be formed) after which the solutions were then left to stand for 10 minutes during which time part of the solid soil separated out on the bottom of the beakers, the remainder being maintained in suspension. The bulk of the suspension was then decanted from each beaker so as to leave the same volume of residual liquid in each and the water was then evaporated to give the cake mix residue.

The beakers plus the residue were weighed, and the beakers were washed out and then re-weighed to give the weight of residue. The test was then repeated reversing the equipment for each product.

Deposition of soil was calculated on the following basis:

$$\text{Redeposition Index} = \frac{\text{\% deposited by test}}{\text{\% deposited by Std}} \times 100$$

$$\text{i.e.} \quad \frac{\dfrac{\text{Amount deposited by test}}{\text{Wt. added to test}}}{\dfrac{\text{Amount deposited by Std}}{\text{Wt. added to Std}}} \times 100$$

On this basis values > 100% indicate that the test product deposits more (i.e. is worse) than the standard, while values < 100% indicate that the test product is superior to the standard. The test is predictive of the ranking of products in terms of their particulate soil suspension capability under normal usage conditions.

Using the above test with Product B forming the standard, Product D gave values of 92% at 0.4% product concentration and 80% at 0.25% product concentration thereby illustrating the particulate soil suspension benefit provided by formulations in accordance with the invention.

Claims

1. A clear homogeneous magnesium containing liquid detergent composition having a chill point of not more than 5°C comprising a surfactant mixture in a hydrotrope-water system, characterised in that the surfactant mixture is formed by the combination of

a) a water soluble C_{13}—C_{18} alkane or C_{12}—C_{16} alkene sulphonate,

b) a water soluble alkyl polyethoxy sulphate wherein the alkyl group contains from 10 to 16 carbon atoms and the polyethoxy group contains an average of from 0.5—6 ethoxy groups,

c) 2.0—5.0% by weight of the composition of an ethoxylated primary C_8—C_{12} alcohol having an HLB in the range 7.5—12.0,

d) 6—18% by weight of the composition of a primary C_{10}—C_{16} alkyl sulphate,

the composition comprising the magnesium ion in an amount corresponding to 0.40X—0.60X, where X is the molar amount of said primary C_{10}—C_{16} alkyl sulphate.

2. A liquid detergent composition according to Claim 1 wherein the ethoxylated alcohol has an HLB in the range 8.0 to 9.5.

3. A liquid detergent composition according to either one of Claims 1 and 2 wherein the alkyl sulphate contains an average of from 12 to 15 atoms in the alkyl chain and is present in an amount of from 8% to 16% by weight of the composition.

4. A liquid detergent composition according to any one of Claims 1—3 further including a suds booster selected from C_{12}—C_{14} mono- and di-C_2—C_3 alkanolamides, C_{12}—C_{14} alkyl amides condensed with up to 15 moles of ethylene oxide per mole of amide and tertiary amine oxides containing a C_8—C_{18} alkyl group.

5. A liquid detergent composition according to either one of Claims 3 and 4 comprising from 8% to 12% by weight of C_{14}—C_{17} alkane sulphonate and from 8% to 12% by weight of C_{12}—C_{13} alkyl polyethoxy sulphate containing an average of two ethoxy groups per mole, wherein the surfactant mixture also comprises from 2.0 to 3.0% by weight of a C_9—C_{11} primary alcohol ethoxylate containing an average of from 2 to 3 ethoxy groups per mole of alcohol.

6. A liquid detergent composition according to either one of Claims 3 and 4 comprising from 4% to 8% by weight of C_{14}—C_{17} alkane sulphonate and from 4% to 8% by weight of C_{13}—C_{15} alkyl polyethoxy sulphate containing an average of two ethoxy groups per mole of alkyl ethoxy sulphate, and from 2% to 4% by weight of a C_9—C_{11} primary alcohol ethoxylate containing an average of 2 to 3 ethoxy groups per mole of alcohol.

7. A liquid detergent composition according to Claim 5 or 6 wherein the alkyl sulphate and the alkyl polyethoxy sulphate are derived from a single alcohol ethoxylate having a mean level of ethoxylation in the range 0.5 to 1.0 moles per mole of alcohol.

Patentansprüche

1. Eine klare, homogene, magnesiumhältige, flüssige Detergenszusammensetzung, die einen Erstarrungspunkt von nicht mehr als 5°C aufweist, enthaltend ein Gemisch oberflächenaktiver Mittel in einem Hydrotrop-Wasser-System, dadurch gekennzeichnet, daß das Gemisch oberflächenaktiver Mittel durch die Kombination von

a) einem wasserlöslichen C_{13}—C_{18}-Alkan- oder C_{12}—C_{16}-Alkensulfonat,

b) einem wasserlöslichen Alkylpolyethoxysulfat, worin die Alkylgruppe 10 bis 16 Kohlenstoffatome enthält, und die Polyethoxygruppe im Durchschnitt 0,5—6 Ethoxygruppen enthält,

c) 2,0—5,0 Gew.-% der Zusammensetzung eines ethoxylierten, primären C_8—C_{12}-Alkohols, der einen HLB-Wert im Bereich von 7,5—12,0 aufweist, und

d) 6—18 Gew.-% der Zusammensetzung eines primären C_{10}—C_{16}-Alkylsulfats gebildet ist,

wobei die Zusammensetzung das Magnesiumion in einer Menge entsprechend 0,40X—0,60X enthält, worin X die molare Menge des genannten primären C_{10}—C_{16}-Alkylsulfats ist.

2. Eine flüssige Detergenszusammensetzung nach Anspruch 1, wobei der ethoxylierte Alkohol einen HLB-Wert im Bereich von 8,0 bis 9,5 aufweist.

3. Eine flüssige Detergenszusammensetzung nach einem der Ansprüche 1 und 2, wobei das Alkylsulfat im Durchschnitt 12 bis 15 Atome in der Alkylkette enthält und in einer Menge von 8 Gew.-% bis 16 Gew.-% der Zusammensetzung vorliegt.

4. Eine flüssige Detergenszusammensetzung nach einem der Ansprüche 1 bis 3, welche weiterhin einen Schaumverstärker enthält, der aus C_{12}—C_{14}-Mono- und Di-C_2—C_3-Alkanolamiden, C_{12}—C_{14}-Alkylamiden, die mit bis zu 15 Mol Ethylenoxid je Mol Amid kondensiert sind, und tertiären Aminoxiden, welche eine C_8—C_{18}-Alkylgruppe enthalten, ausgewählt ist.

5. Eine flüssige Detergenszusammensetzung nach einem der Ansprüche 3 und 4, enthaltend 8 Gew.-% bis 12 Gew.-% C_{14}—C_{17}-Alkansulfonat und 8 Gew.-% bis 12 Gew.-% C_{12}—C_{13}-Alkylpolyethoxysulfat mit im Durchschnitt zwei Ethoxygruppen je Mol, wobei das Gemisch oberflächenaktiver Mittel auch 2,0 bis 3,0 Gew.-% eines C_9—C_{11}-primären Alkoholethoxylats enthält, welches im Durchschnitt 2 bis 3 Ethoxygruppen je Mol Alkohol aufweist.

6. Eine flüssige Detergenszusammensetzung nach einem der Ansprüche 3 und 4, enthaltend 4 Gew.-% bis 8 Gew.-% C_{14}—C_{17}-Alkansulfonat und 4 Gew.-% bis 8 Gew.-% C_{13}—C_{15}-Alkylpolyethoxysulfat mit im Durchschnitt 2 Ethoxygruppen von Alkylethoxysulfat je Mol, und 2 Gew.-% bis 4 Gew.-% eines C_9—C_{11}-primären Alkoholethoxylats, das im Durchschnitt 2 bis 3 Ethoxygruppen je Mol Alkohol aufweist.

7. Eine flüssige Detergenszusammensetzung nach Anspruch 5 oder 6, wobei das Alkylsulfat und das Alkylpolyethoxysulfat von einem einzigen Alkoholethoxylat abgeleitet sind, das einen mittleren Ethoxylierungsgrad im Bereich von 0,5 bis 1,0 Mol je Mol Alkohol aufweist.

Revendications

1. Une composition détergente liquide, homogène, limpide contenant du magnésium ayant un point de trouble non supérieur à 5°C comprenant un mélange tensioactif dans un système hydrotrope-eau, caractérisée, en ce que le mélange tensioactif est formé par la combinaison

a) d'un alcane C_{13}—C_{18} ou alcène C_{12}—C_{16} sulfonate soluble dans l'eau,

b) d'un alkyl polyéthoxysulfate soluble dans l'eau dans lequel le groupe alkyle contient 10 à 16 atomes de carbone et le groupe polyéthoxy contient en moyenne 0,5 à 6 groupes éthoxy,

c) de 2,0 à 5,0% en poids, par rapport à la composition, d'un alcool primaire en C_8 à C_{12} éthoxylé possédant une HLB comprise dans la gamme de 7,5 à 12,0,

d) de 6 à 18% en poids, par rapport à la composition, d'un alkyl C_{10}—C_{16} sulfate primaire,

la composition renfermant l'ion magnésium en une quantité correspondant à 0,40X—0,60X où X est la quantité molaire dudit alkyl C_{10}—C_{16} sulfate primaire.

2. Composition détergente liquide selon la revendication 1, dans laquelle l'alcool éthoxylé possède une HLB comprise dans la gamme de 8,0 à 9,5.

3. Composition détergente liquide selon l'une des revendications 1 et 2, dans laquelle l'alkylsulfate contient une moyenne de 12 à 15 atomes dans la chaîne alkyle et est présent à raison de 8% à 16% en poids de la composition.

4. Composition détergente liquide selon l'une quelconque des revendications 1 à 3, contenant en outre un renforçateur de mousse choisi parmi des mono- alcanolamides en C_{12} à C_{14} et des di- alcanolamides en C_2 à C_3, des alkyl C_{12}—C_{14} amides condensés avec jusqu'à 15 moles d'oxyde d'éthylène par mole d'amide et des oxydes d'amines tertiaires contenant un groupe alkyle en C_8 à C_{18}.

5. Composition détergente liquide selon l'une des revendications 3 et 4 renfermant 8% à 12% en poids d'un alcane C_{14}—C_{17} sulfonate et 8% à 12% en poids d'un alkyl C_{12}—C_{13} polyéthoxysulfate contenant en moyenne deux groupes éthoxy par mole, dans laquelle le mélange tensioactif contient également 2,0 à 3,0% en poids d'un éthoxylat d'alcool primaire en C_9 à C_{11} renfermant en moyenne 2 à 3 groupes éthoxy par mole d'alcool.

6. Composition détergente liquide selon l'une des revendications 3 et 4 renfermant 4% à 8% en poids d'un alcane C_{14}—C_{17} sulfonate, 4% à 8% en poids d'un alkyl C_{13}—C_{15} polyéthoxysulfate contenant en moyenne deux groupes éthoxy d'alkyl éthoxysulfate par mole et 2% à 4% en poids d'un éthoxylat d'alcool primaire en C_9 à C_{11} renfermant en moyenne 2 à 3 groupes éthoxy par mole d'alcool.

7. Composition détergente liquide selon la revendication 5 ou 6, dans laquelle l'alkylsulfate et l'alkyl polyéthoxysulfate dérivent d'un seul alcool éthoxylé avec un degré d'éthoxylation moyen entre 0,5 et 1 mole par mole d'alcool.